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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 30 April 2004		3. REPORT TYPE AND DATES COVERED <b>FINAL</b> 5 November 1998 through 31 Dec 2003
4. TITLE AND SUBTITLE Final Progress Report: Investigation of Nanophase Materials for Thermoelectric Applications (11/05/1998-12/31/2003)			5. FUNDING NUMBERS G. DAAD19-99-1-0001	
6. AUTHOR(S) Kevin L. Stokes and Charles J. O'Connor				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Advanced Materials Research Institute University of New Orleans New Orleans, LA 70148			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER 39197-MS •7	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The goal of this research project is to develop an understanding of transport properties in nanometer-scale materials and to determine if engineering a material structure using nanometer-sized particles as building blocks can increase the intrinsic thermoelectric efficiency. The project involved a close collaboration between the University of New Orleans and IBM T.J. Watson Research Center. Our major accomplishments include the chemical synthesis of nanoparticles, nanorods and nanowires of lead chalcogenide, bismuth chalcogenide and bismuth antimony materials. We have also formed semiconductor nanoparticle/conducting polymer nanocomposites and studied the thermoelectric properties of these materials. We have also made contributions to new, pressure-dependent thermoelectric transport measurement techniques and chemical techniques for creating ordered nanoparticle assemblies consisting of two different nanoparticle materials.				
14. SUBJECT TERMS Semiconductor nanoparticles, thermoelectric materials			15. NUMBER OF PAGES 15	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL	

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**FINAL PROGRESS REPORT – Investigation of Nanophase Materials for  
Thermoelectric Applications (11/05/1998-12/31/2003)**

**1. TABLE OF CONTENTS**

1.	TABLE OF CONTENTS .....	1
2.	STATEMENT OF THE PROBLEM .....	2
3.	SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS .....	2
	3.1 Summary .....	2
	3.2 Lead chalcogenide core/shell nanowires.....	3
	3.3 Bismuth-antimony alloy nanoparticles .....	4
	3.4 Bismuth sulfide/telluride nanorods .....	6
	3.5 Binary nanoparticle superlattices.....	7
	3.6 Semiconductor/polymer nanocomposites .....	7
	3.7 Transport measurements .....	8
	3.8 Thermoelectric properties of composites (theory).....	10
	3.9 Test and measurement apparatus .....	11
4.	PUBLICATIONS.....	12
5.	SCIENTIFIC PERSONNEL .....	14
6.	INVENTIONS .....	15

## **2. STATEMENT OF THE PROBLEM**

Compact, solid-state thermoelectric devices are used for both cooling and power generation. These highly reliable devices have no moving parts, operate around room temperature, and are easily integrated into compact systems. Despite these advantages, engineering applications have been limited by the relatively low intrinsic power conversion efficiency of the semiconductor materials used in these devices. The intrinsic thermoelectric efficiency for a given material is defined by the unitless figure of merit,  $ZT$ ,

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_g} \quad (1)$$

where  $S$  is the Seebeck coefficient,  $\sigma$  the electrical conductivity,  $T$  is the absolute temperature, and  $\kappa_e$  and  $\kappa_g$  are the electronic and lattice contributions to the thermal conductivity, respectively. Engineered material structures, in which at least one dimension is on the nanometer scale, dramatically alter the thermoelectric properties due to the confinement of the carriers inside the material and phonon scattering from nanometer-scale interfaces. Under confinement, the Seebeck coefficient can increase as a result of the increase in the density of states near the Fermi energy and the lattice thermal conductivity,  $\kappa_g$ , will decrease due to increased phonon scattering at boundaries (relative to electron scattering). Thermoelectric materials with enhanced performance ( $ZT > 1$ ) have recently been realized in nanometer-scale heterogeneous semiconductor material systems. This project investigates the use of chemically synthesized semiconductor nanoparticles as building blocks to engineer composite materials with enhanced thermoelectric performance. We have investigated methods synthesizing various semiconductor compounds in nanoscale form (spherical particles, rods and wires), arranging nanoparticles in ordered arrays and forming composites with nanoparticles and conducting polymers.

## **3. SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS**

### **3.1 Summary**

The goal of this research project was to increase the understanding of transport properties in nanometer-scale materials and determine if the intrinsic thermoelectric efficiency can be increased by engineering a material structure using nanometer-sized particles as building blocks. The project consists of four parts: 1) the synthesis of semiconductor and semimetal nanoparticles 2) the consolidation of the particles into ordered arrays, colloidal crystals and other functional materials, 3) accurate measurements of the composite material's thermophysical properties and 4) theoretical modeling of the transport phenomena. The project involves a close collaboration between the University of New Orleans and IBM T.J. Watson Research Center. Our nanoparticle synthesis efforts have been directed toward the lead chalcogenides (IBM) and the bismuth chalcogenides (UNO). We have been successful in synthesizing PbTe/PbSe core-shell nanowires as well as nanowires of PbTe, PbSe, and PbS. This is one of the primary goals of this program.

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We have synthesized  $\text{Bi}_2\text{S}_3$  and  $\text{Bi}_2\text{Te}_3$  nanostructures (particles and rods) and formed composite materials by combining these semiconductor nanostructures with a conducting polymer. In addition, we have been successful. We have measured the thermal and electrical properties of sintered films, pressed pellets and polymer/semiconductor nanocomposites. Finally, we have developed a theory for the bulk (composite) electronic and thermal transport in nanoparticle core/shell structures and superlattices of core/shell nanowires.

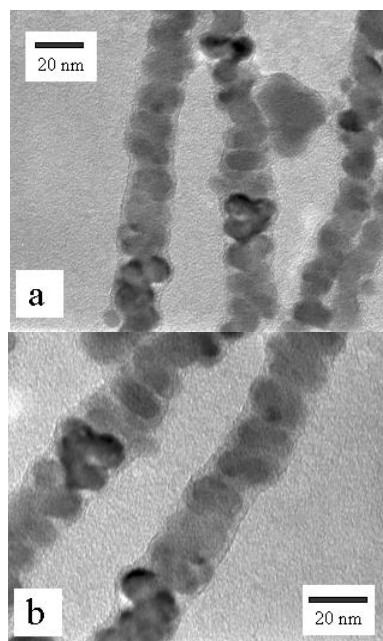
*Key Accomplishments*

- Synthesized highly-crystalline, nanoparticles colloids of PbSe, PbTe and PbS with a nearly monodisperse distribution of particle sizes. The physical properties and morphology of this material has been completely characterized. We demonstrated that we can control the morphology of these nanostructures from spherical to cubic particles and nanowires.
- Synthesized highly-crystalline, nearly monodisperse colloids of bismuth sulfide and bismuth telluride compounds and are able to form rods with controlled morphology.
- Developed techniques for ordered self assembly of nanoparticle systems consisting of two different nanoparticle materials.
- Performed transport measurements on sintered nanoparticle films and nanoparticle conducting polymer/nanoparticle composites.
- Measured current-voltage characteristics of single PbTe nanowires.
- Measurement the thermoelectric properties of state-of-the-art semiconductor materials (clathrate, perovskite, carbon nanotube composites, and nanoparticle/polymer composites) as a function of temperature and hydrostatic pressure.

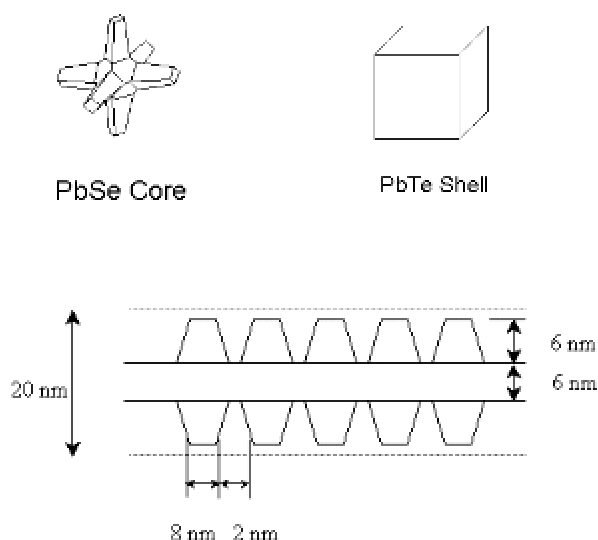
### *3.2 Lead chalcogenide core/shell nanowires*

One of the main accomplishments of this project, and in fact, a primary goal of this research project was the successful synthesis of PbTe/PbSe core/shell nanowires. These nanowire structures are shown in Figure 1. These structures are formed from modifications of the high-temperature organometallic chemical synthesis procedures described in previous reports and journal articles. We can control the core/shell structure morphology (cubes, spheres, stars, and nanowires) and have added the sulfur compound of this family (PbS) to our list of lead chalcogenide nanostructures.

A model for the formation of the PbSe/PbTe core shell nanowires is shown in Figure 2. First the PbSe core compound is formed. Under precisely-defined conditions, this compound forms as a star-shaped structure with six arms. The arms of these structures connect to form a chain of PbSe stars. Then, the tellurium precursor is added to the solution. PbTe fills in around the PbSe stars. The TEM image (Figure 1) shows, however, that the chains of PbSe stars that form the core are not completely connected. Also, this nanowire formation is always accompanied by a number of PbTe cubic nanoparticles which must be separated by centrifugation or filtering.



**Figure 1.** Transmission electron microscope images of PbTe/PbSe core/shell nanowires. The darker structures are PbSe cores surrounded by a coating of PbTe.



**Figure 2.** Simple model of PbSe/PbTe core/shell nanowire growth.

A model for the formation of the PbSe/PbTe core shell nanowires is shown in Figure 2. First the PbSe core compound is formed. Under precisely-defined conditions, this compound forms as a star-shaped structure with six arms. The arms of these structures connect to form a chain of PbSe stars. Then, the tellurium precursor is added to the solution. PbTe fills in around the PbSe stars. The TEM image (Figure 1) shows, however, that the chains of PbSe stars that form the core are not completely connected. Also, this nanowire formation is always accompanied by a number of PbTe cubic nanoparticles which must be separated by centrifugation or filtering.

### 3.3 Bismuth-antimony alloy nanoparticles

Highly crystalline, bismuth and bismuth-antimony alloy nanoparticles were synthesized using a high-temperature, organic solution phase reduction method. The nanoparticles are capped by a carboxylic acid molecule and form stable colloids in nonpolar solvents. Size-selective precipitation of the original colloid results in colloids with a narrow size distribution of inorganic particles. Upon evaporation of the solvent, these particles can be made to organize into two-dimensional assemblies with short-range hexagonal order. Two examples are shown in Fig. 4, Bi and Bi<sub>0.9</sub>Sb<sub>0.1</sub>.

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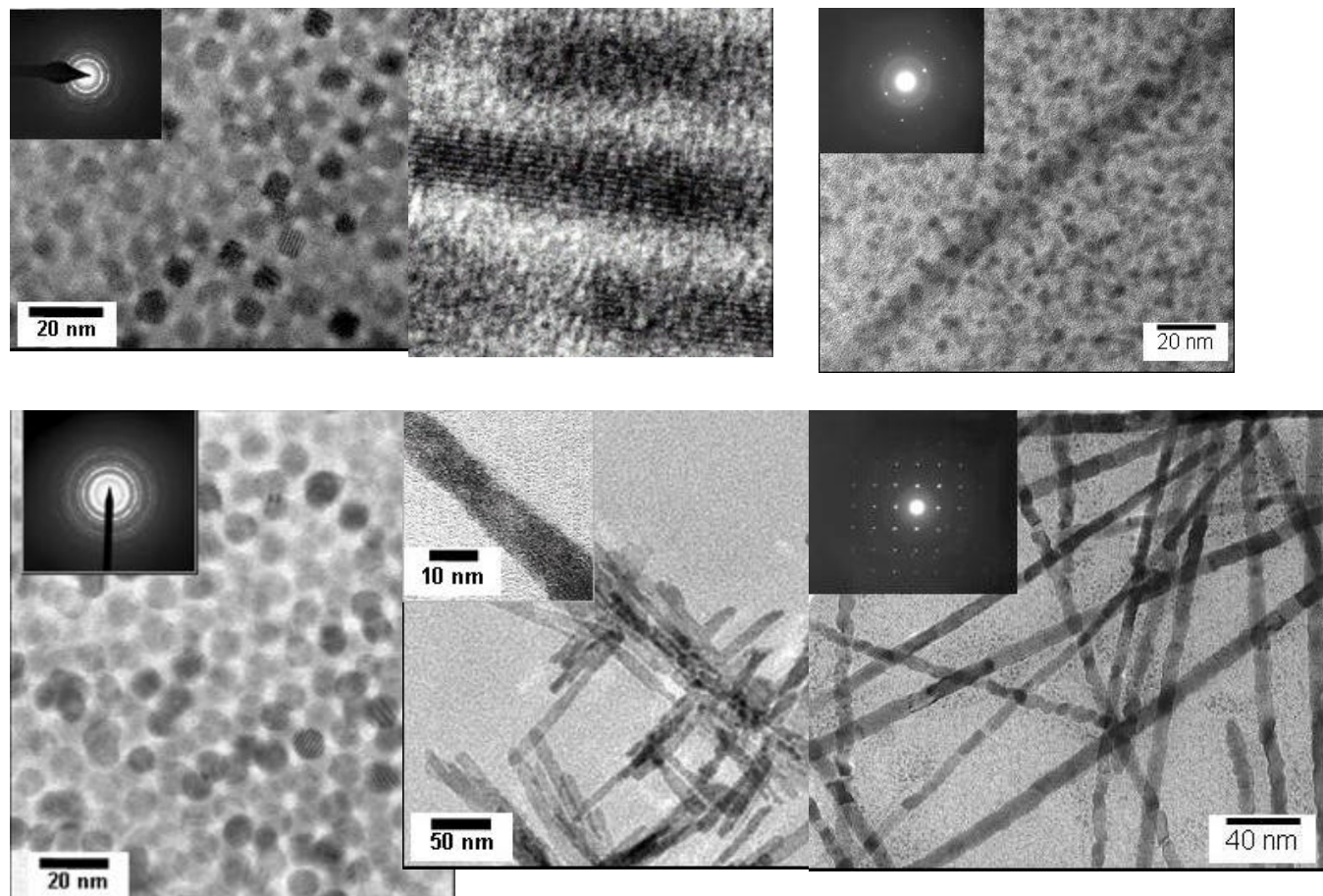


Figure 3. Transmission electron microscope images of nanoparticles, nanorods and nanowires of PbTe (top row) and PbS (bottom row).

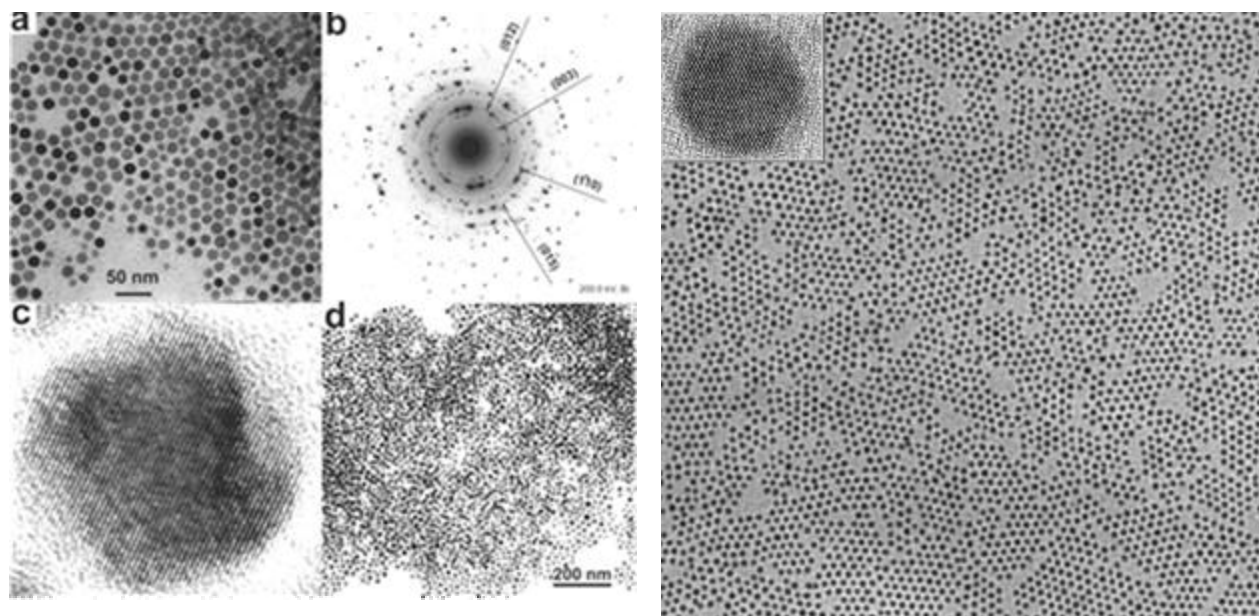


Figure 4. *Left* – Bismuth nanoparticles with diameter of ~6 nm. *Right* – Bismuth-antimony nanoparticles with diameter of ~8 nm. The antimony concentration is 10%. The inset shows a high-resolution TEM image of a single nanoparticle demonstrating distinct fringes from well-organized lattice planes.

### 3.4 Bismuth sulfide/telluride nanorods

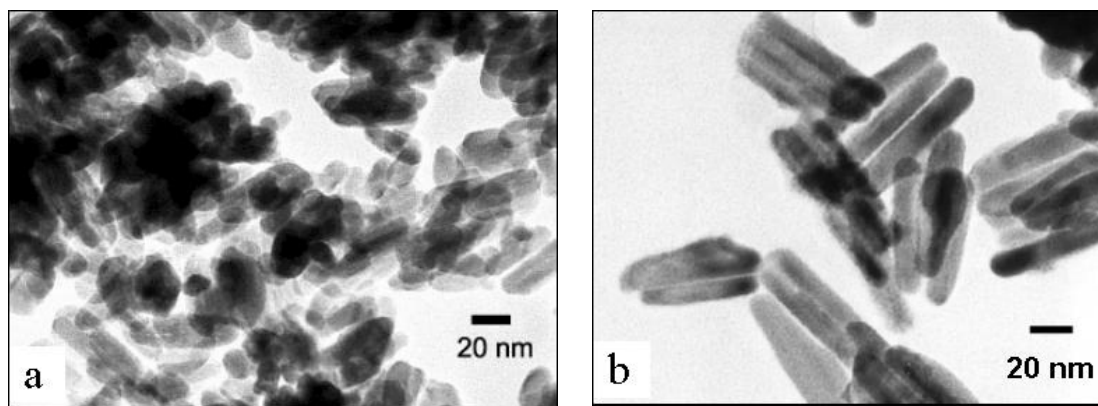


Figure 5. Transmission electron microscope images of bismuth sulfide nanorods synthesized under different reaction conditions. (a) synthesized with a carboxyl stabilizing agent ( $-\text{COO}^-$ ) and (b) synthesized with a sulfonate stabilizing agent ( $-\text{SO}_3^-$ ).

Highly crystalline, bismuth sulfide nanorods (oblate nanoparticles) were synthesized using still another variation of the high-temperature, organic solution phase reduction method. The chemical reaction is a co-precipitation using bismuth 2-ethylhexanoate (Bi) and thioacetamide (S) in the presence of appropriate organic capping agents. The Bi:S ratio can be controlled by varying the ratio of the two precursors. The aspect ratio and size of the particle are controlled by

adjusting the reaction time and temperature and organic capping ligand. Figure 3 shows the results of the bismuth sulfide synthesis using two different capping ligands.

### 3.5 Binary nanoparticle superlattices

An important advance in nanoparticle assembly is the fabrication of a *binary* three-dimensional assembly of 11 nm  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and 6 nm PbSe nanoparticles, the results of which are shown in Fig. 6. This work demonstrates the controlled assembly of two very different nanoparticle compounds, with of course, different optical and magnetic properties. We point out that this research effort was a collaboration between Columbia, IBM and AMRI at the University of New Orleans. The work was performed, in part, by AMRI post-doc K.-S. Cho while at IBM, T.J. Watson Research Center, under the direction of Dr. Chris Murray.

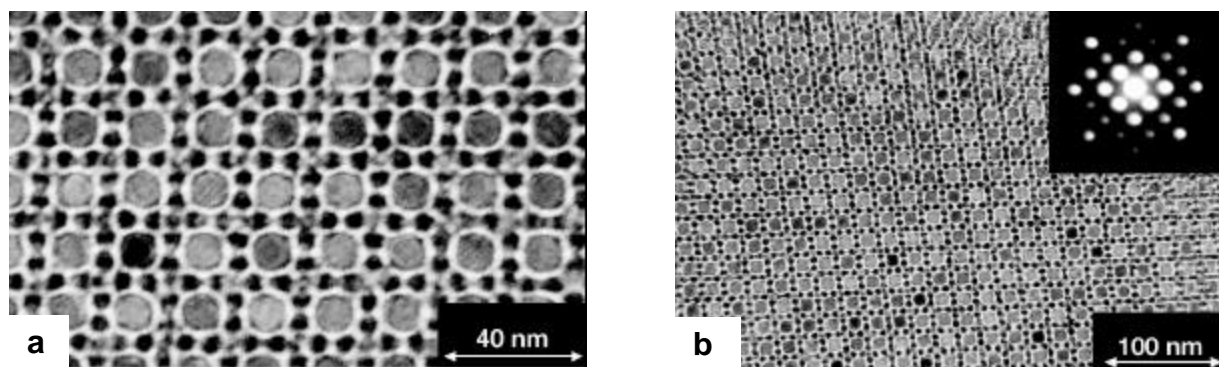


Figure 6. Transmission electron micrographs showing a three dimensional, binary ordered self assembly of 11 nm  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and 6 nm PbSe nanoparticles, from Ref. {Redl, 2003 #84}. a) High magnification image of the [100] superlattice plane, and b) low magnification image, as in a); inset shows a small-angle electron diffraction pattern of a 6- $\mu\text{m}^2$  area of the superlattice.

### 3.6 Semiconductor/polymer nanocomposites

Successful growth of bismuth sulfide and bismuth telluride in nanorod form has allowed the formation of a core-shell particle, which utilizes the bismuth compound as a quantum confining core and conducting polyaniline as the outer shell. A bulk form of the core-shell system has been fabricated through pressing and sintering techniques which has resulted in a nanocomposite of nanorod core particles within a polyaniline matrix. Three-dimensional quantum confinement of the carriers within the bismuth compound is obtained through the higher polymer bandgap as well as complete nanorod surface coverage.

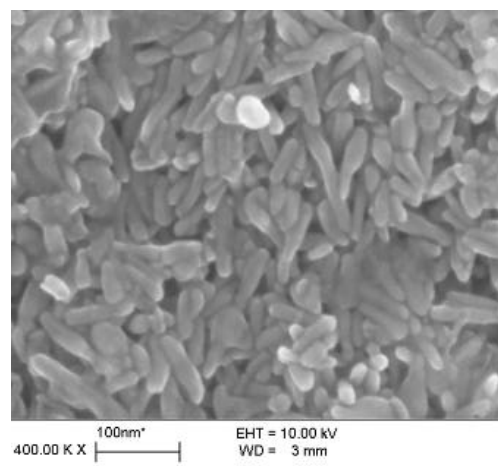
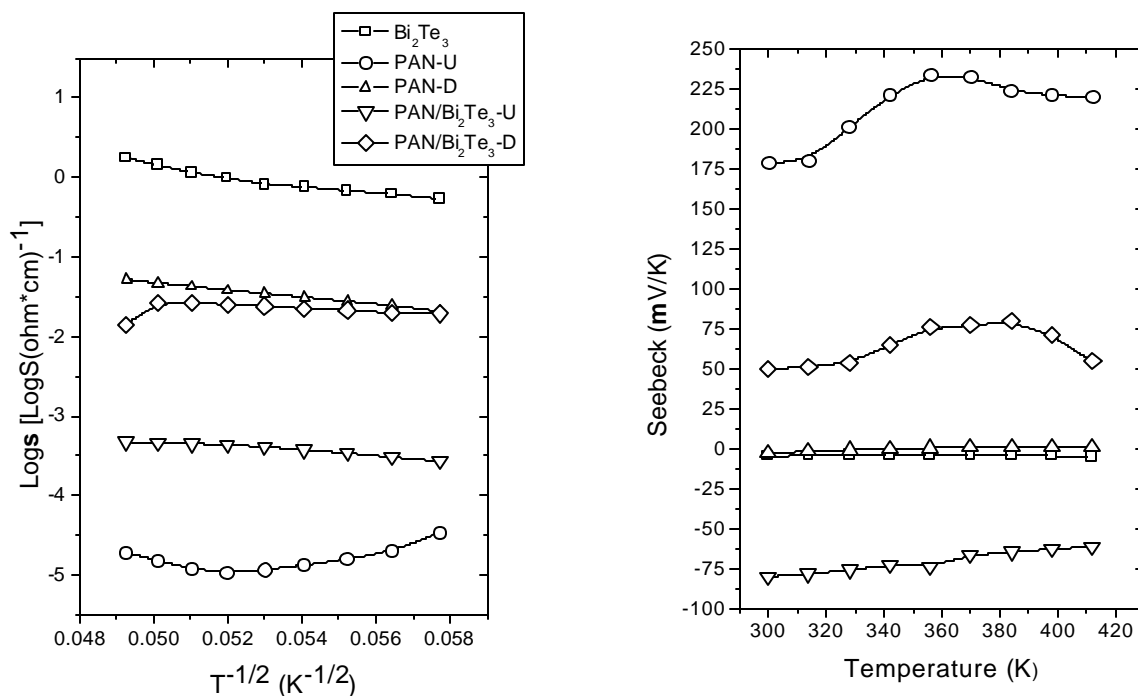


Figure 7. Bi<sub>2</sub>S<sub>3</sub>-polyaniline nanocomposite after compaction.



**REPORT DOCUMENTATION PAGE (SF298)**  
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Electrical conductivity of polymer is controlled by protonation of the polyaniline in HCl vapor. Both the electrical conductivity and Seebeck coefficient of the composite is also found to be responsive to doping levels of the outer polymer shell.



**Figure 8. Thermoelectric properties of bismuth telluride/polyaniline nanocomposites as a function of temperature.**

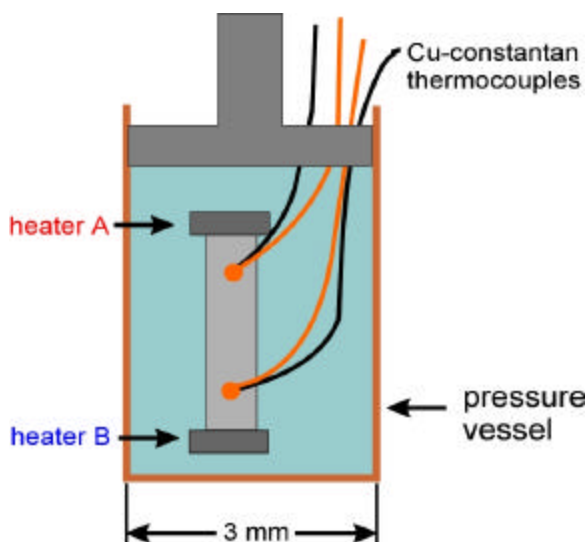
Our complete sample sets developed for this project work consist of, single compound nanorods and nanocomposites and polyaniline (PAN), for comparison. Specifically, the thermoelectric coefficients were obtained for the doped (D) and undoped (U) PAN as well as coated and uncoated  $\text{Bi}_2\text{S}_3$  and  $\text{Bi}_2\text{Te}_3$  nanorods. In all cases, powders were isolated, compressed in a uniaxial cold press and then sintered at temperatures  $< 150^\circ\text{C}$ . Figure 7. shows Seebeck coefficient and electrical conductivity for five samples of  $\text{Bi}_2\text{Te}_3$ /polyaniline nanocomposite. In these studies,  $\text{Bi}_2\text{Te}_3$  nanorods were chemically-synthesized using the high-temperature, organometallic methods outlined above. Currently, this latest  $\text{Bi}_2\text{Te}_3$  work is being written up and will be submitted to a scientific journal.

### 3.7 Transport measurements

During the course of this project, we adapted and developed a method for making temperature-dependent Seebeck and electrical conductivity measurements under hydrostatic pressure. A small vessel was machined from a beryllium-copper alloy. The sample two small (0.002" diameter) copper-constantan thermocouples were attached to the sample, as illustrated in Fig. 8.

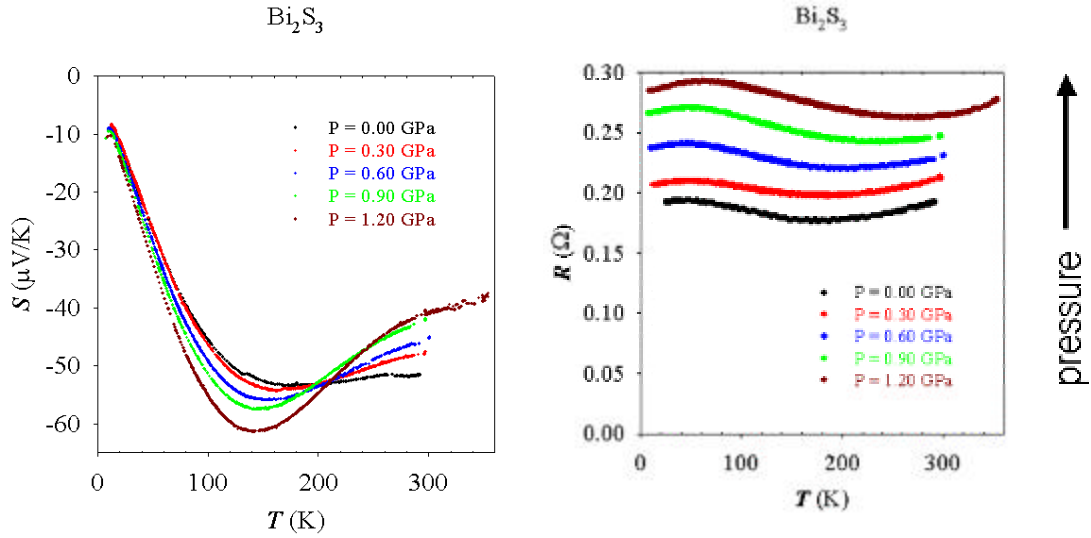
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Two ceramic, surface mount resistors were attached to the ends of the sample as heaters. In addition, two current leads (not shown) were attached to the ends of the sample. This assembly was placed in a small, deformable, sealed tube filled with a pressure transmitting medium, Fluorinert. This tube was placed into the Be-Cu vessel and the upper piston was compressed using a hydraulic press. The piston was then mechanically locked in place. The entire apparatus could then be cooled by simply placing it in a liquid nitrogen bath. The two heaters were driven with balanced sine-wave currents,  $90^\circ$  out of phase which yields periodic heating of the sample ends,  $180^\circ$  out of phase. The Seebeck and IR voltages are measured from the copper leads. The system is capable of attaining pressures up to 2 GPa.



**Figure 9.** Diagram of the vessel used for the pressure dependent thermoelectric measurements.

We performed several pressure-dependent transport studies during the course of this project, studying such diverse materials as semiconductor nanocomposites, clathrates,  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ , and carbon nanotubes. Figure 9 shows results for bismuth sulfide nanoparticle material. As mentioned above, our nanoparticles were formed into continuous structures two ways: 1) deposition onto an insulating substrate from solution and subsequent evaporation of the solvent to form thin films and 2) uniaxial compaction of the dried powder followed by low-temperature sintering ( $\sim 100^\circ\text{C}$  to  $300^\circ\text{C}$ ). For bismuth sulfide, the best materials were formed by compaction of the powder under moderate pressures (70 MPa) at  $300^\circ\text{C}$  under vacuum. The material was then sintered at ambient pressure under vacuum at  $200^\circ\text{C}$  to  $250^\circ\text{C}$  for several hours. Transport measurements (Seebeck coefficient and resistivity) as a function of temperature for these materials is shown in Figure 9. At ambient pressure, the Seebeck coefficient is a monotonically increasing function of temperature. At higher pressures, a pronounced dip in the Seebeck coefficient forms at about 140 K, which increases with increasing pressure. This is assumed to be due to the different influence of carriers from different bands. The resistivity, however, increases with increasing pressure, but retains the same temperature dependence. Both the Seebeck coefficient and resistivity return to within 15% of their initial ambient pressure values after temperature cycling.



**Figure 10. Transport property measurements of sintered 4 nm  $\times$  40 nm nanorods of  $\text{Bi}_2\text{S}_3$  under hydrostatic pressure.**

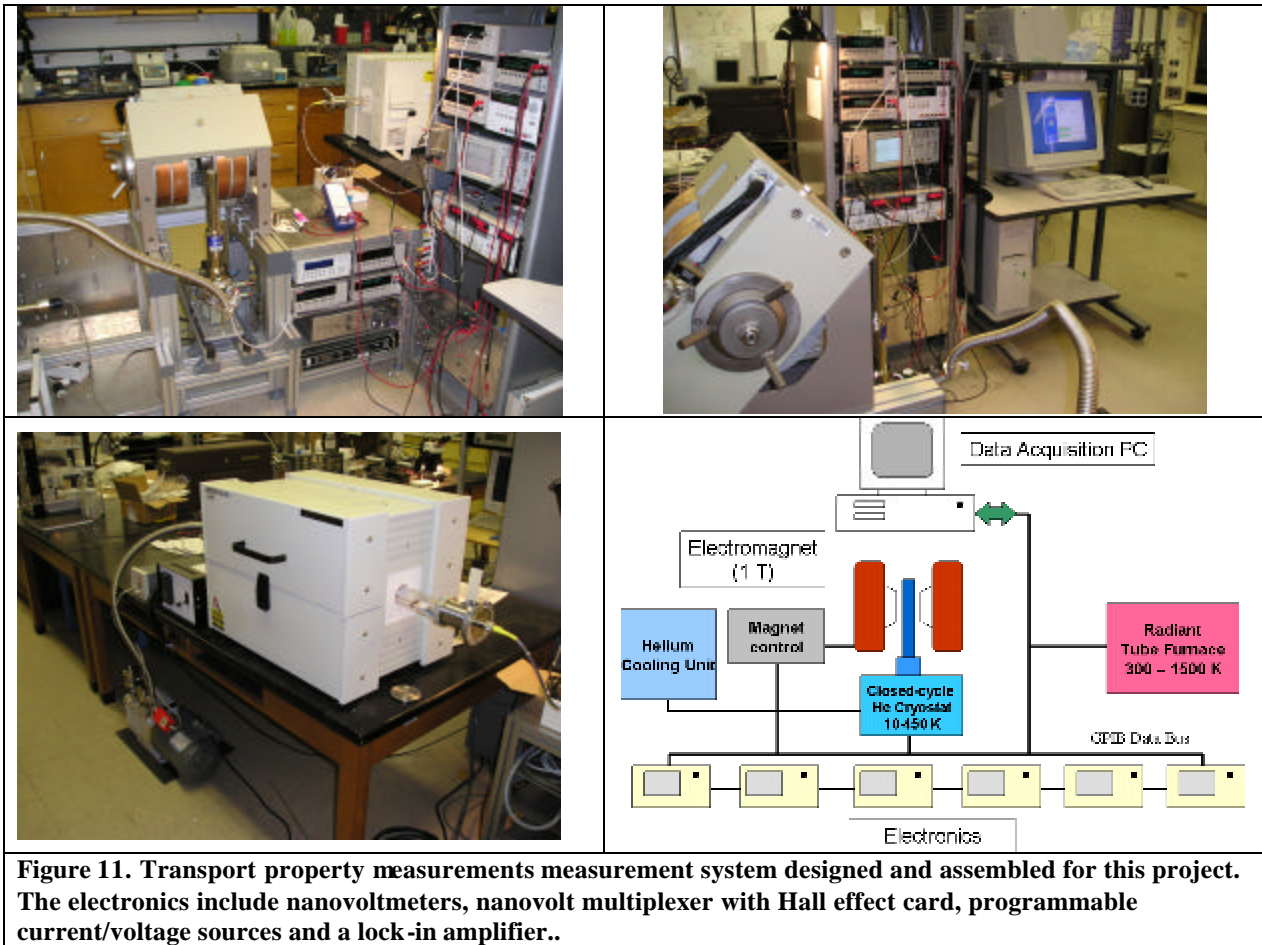
### 3.8 Thermoelectric properties of composites (theory)

The successful fabrication of a nanocomposite in bulk form consisting of a randomly oriented assembly of nanoscale sized core-shell particles has required an increased understanding of the theoretical aspects of the thermoelectric transport properties. Specifically, we wanted to develop a model for the nanocomposite which consists of a nanorod core in 1D quantum confinement coated with an outer conducting polymer shell. Upon fabrication of these composites, the nanorods are embedded within a three-dimensional conducting polymer matrix. We address the nanorod thermoelectric components by assuming a single parabolic band within the one-dimension density of states. Both elastic and inelastic scattering of electrons or holes is accommodated by solving the variational form of the Boltzmann transport equation. An altered lattice thermal conductivity for the confined nanorods is calculated separately to account for boundary scattering that is important in low dimension structures. The thermal and electrical properties of the conducting polyaniline shell (matrix) were modeled using temperature-dependent phenomenological models. Exact expressions for the bulk effective electrical and thermal conductivities, Seebeck coefficient and figure of merit are then obtained through the field decoupling transformation, which is a special case of two-component composites. The method we developed is easily generalized to any two-component composite of spherical or cylindrical microstructure and is independent of the materials bulk geometry. The results similarly apply to one, two or three dimensional transport regimes with or without quantum confinement merely by solving the appropriate fundamental transport equations for each constituent material. Comparison to experimental data is then presented which helps validate the nanocomposite theory.

**REPORT DOCUMENTATION PAGE (SF298)**  
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### 3.9 Test and measurement apparatus

Finally, we describe the measurement apparatus that was constructed for this project. The shown in Fig. 10, was made to be extremely flexible. It is built around two temperature-controlled chambers: 1. a closed cycle, He cryostat for temperatures from 10 K to 450 K and 2. a tube furnace for temperatures from  $\sim 300$  K to 1500 K. Both chambers are capable of achieving moderate vacuum ( $10^{-6}$  to  $10^{-5}$  Torr). The electronic instrumentation is shared between the two temperature controlled chambers. This electronics, with the computer, allows us to measure Seebeck coefficient (standard and ac), electrical conductivity, and thermal conductivity (steady-state, ac and  $3\omega$ ). In addition, the sample mounted in the cryostat can be placed between the poles of the computer-controlled electromagnet for Hall effect measurements.



**REPORT DOCUMENTATION PAGE (SF298)**  
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#### 4. PUBLICATIONS

*(a) Papers published in peer-reviewed journals*

- W.L. Zhou, J. He, J. Fang, T.-A. Huynh, T.J. Kennedy, K.L. Stokes and C.J. O'Connor, "Self assembly of FePt nanoparticles into nanorings," *J. Appl. Phys.* **93**:7340 (2003).
- F. X. Redl, K.-S. Cho, C.B. Murray and S. O'Brien, "Three-dimensional binary superlattices of magnetic nanocrystals and semiconductor quantum dots," *Nature* **423**:968-971 (2003).
- F. Chen, K.L. Stokes and R. Funahashi, "Thermoelectric Properties of  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$  Whiskers Under Hydrostatic Pressure," *Appl. Phys. Lett.* **81**:2379-2381 (2002).
- J. Fang, L.D. Tung and K.L. Stokes et al. "Synthesis and magnetic properties of CoPt poly(methylmethacrylate) nanostructured composite material," *J. Appl. Phys.* **91**:8816 (2002).
- C. B. Murray, S. Sun, W. Gaschler, H. Doyle, T. A. Betley and C. R. Kagan, "Colloidal synthesis of nanocrystals and nanocrystal superlattices," *IBM J. Res. & Dev.* **45**:47-56 (2001).
- F. Chen, K.L. Stokes and G.S. Nolas, "Thermoelectric properties of tin clathrates under hydrostatic pressure," *J. Phys. Chem. Solids* **63**:827 (2002).
- J. Fang, K.L. Stokes, W.L. Zhou, W. Wang and J. Dai, "Self assembled bismuth nanocrystallites," *Chem. Comm.* **18**:1872 (2001).
- W.L. Zhou, J.A. Weimann, K.L. Stokes and C.J. O'Connor, "Monodisperse PbSe nanoparticle self-assembling nanoarrays before and after annealing," *J. Microscopy and Microanalysis* **7**:314 (2001).
- J. Fang, K.L. Stokes, J.A. Weimann, W.L. Zhou, J. Dai, F. Chen and C.J. O'Connor, "Microemulsion-processed bismuth nanoparticles," *Mater. Sci. Engineer. B* **56**:1001 (2000).
- J. Fang, K.L. Stokes, J.A. Weimann and W. Zhou, "Nanocrystalline bismuth synthesized via an in situ polymerization-microemulsion process," *Mater. Lett.* **42**:113 (2000).

*(b) Papers published in conference proceedings*

- P.L. Garrity and K.L. Stokes, "A Variational Solution of the Thermoelectric Transport Properties of Two-Component Nanocomposite Systems," *Mat. Res. Soc. Symp. Proc. Vol. 793, Thermoelectric Materials 2003 - Research and Applications*, G.S. Nolas et al., ed. (MRS, Warrendale, PA, 2004) p. S5.5.
- V.B. Reddy, P.L. Garrity, and K.L. Stokes, "Synthesis and Characterization of Bismuth Sulfide and Bismuth Telluride Nanorods and their Polyaniline Nanocomposites," *Mat. Res. Soc. Symp. Proc. Vol. 793, Thermoelectric Materials 2003 - Research and Applications*, G.S. Nolas et al., ed. (MRS, Warrendale, PA, 2004) p. S8.36.
- F. Chen, Y. Y. Xue, K. L. Stokes, H. Wang and C. W. Chua, "Transport Properties For Carbon Nanotubes Under Hydrostatic Pressure," *Nanotech2003 Vol. 1* (NTSI, Cambridge, MA, 2003) pp. 144-147.
- F. Chen, K.L. Stokes, W. Zhou and J. Fang, "Synthesis and properties of lead selenide nanocrystal solids," in *Thermoelectric Materials 2001*, Mat. Res. Soc. Symp. Proc. **691**, ed. By G.S. Nolas et al. (2002) G10.2.

**REPORT DOCUMENTATION PAGE (SF298)**  
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- J. Fang, K.L. Stokes, J. He and C.J. O'Connor, "Pattern Shape-Controlled Self-Assembly of  $\text{Bi}_{0.9}\text{Sb}_{0.1}$  Nanocrystallites," in *Thermoelectric Materials 2001*, Mat. Res. Soc. Symp. Proc. **691**, ed. By G.S. Nolas et al. (2002) G10.3.
- F. Chen, K.L. Stokes and G.S. Nolas, "Pressure Effect of Seebeck Coefficient for Zinc-doped Tin Clathrates," in *Thermoelectric Materials 2001*, Mat. Res. Soc. Symp. Proc. **691**, ed. By G.S. Nolas et al. (2002) G4.4.
- J. Fang, F. Chen, K.L. Stokes, J. He, J. Tang and C.J. O'Connor, "Synthesis and Thermoelectric Properties of  $\text{Bi}_2\text{S}_3$  Nanobeads," in *Materials for Energy Storage, Generation and Transport*, Mat. Res. Soc. Symp. Proc. **730**, ed. by G. Ceder et al. (2002) V5.5.
- J. Fang, K.L. Stokes, W. L. Zhou, C. B. Murray and C.J. O'Connor, "Nanometer-sized Bismuth Crystallites Synthesized from a High-temperature Reducing System," in *Synthesis, Functional Properties and Applications of Nanostructures*, Mat. Res. Soc. Symp. Proc. **676**, ed. by H.W. Hahn et al. (2002) Y8.9.
- J. Fang, K.L. Stokes, W. Zhou, J.A. Wiemann, J. Dai and C.J. O'Connor, "Colloidal bismuth nanoparticles: Synthesis and UV-Vis absorption," Proceedings of ISCANI (International Symposium on Cluster and Nanostructure Interfaces), ed. By P. Jena, World Scientific Publishing, Singapore (2000).
- K.L. Stokes, J. Fang and C.J. O'Connor, "Synthesis and properties of Bi nanoparticles," in *Proc. XVIII Internation.Conf. on Thermoelectrics* (1999).
- K.L. Stokes, A.C. Ehrlich and G.S. Nolas, "Thermal conductivity of Fe-doped  $\text{CoSb}_3$  skutterudites," in *Thermoelectric Materials 1998*, Mat. Res. Soc. Symp. Proc. **545**, ed by T.M. Tritt et al. (1999).

**(c) Papers presented at meetings**

- "Thermoelectric Properties of Bismuth Sulfide Nanocomposites," Pat Garrity, Ven Reddy and Kevin Stokes\*, Louisiana Materials Research and Development Conference, Lafayette, LA, November 4-5, 2003.
- "Thermoelectric Properties of Bismuth Sulfide Nanocomposites," Pat Garrity and Kevin Stokes\*, American Filtration Society, Ann Arbor, MI, October 2, 2003. (invited)
- "Synthesis of PbSe, PbS, PbTe Nanocrystals (From Quantum Dots to Nanowires)," C.B.Murray, K.-S. Cho and W. Gaschler, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003.
- "PbSe Quantum Dots and Quantum Cubes," K.-S. Cho, C.B. Murray and K.L. Stokes, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003.
- "Progress in Nanophase Thermoelectrics," K.L. Stokes, V. Reddy, P. Garrity, F. Chen, K.-S. Cho and C.B. Murray, Presented at the 6th Annual DARPA-AMRI-Industry Symposium, New Orleans, LA. February 2003.
- "High Temperature Synthesis of Bismuth Chalcogenides," V. Reddy, P. Garrity and K.L. Stokes, Poster presented at the 6th Annual DARPA-AMRI-Industry Symposium, New Orleans, LA. February 2003.
- "Shape Evolution of PbSe Quantum Dots and Nanowires," K.-S. Cho, W. Gaschler, C.B. Murray and K.L. Stokes, Poster presented at the 6th Annual DARPA-AMRI-Industry Symposium, New Orleans, LA. February 2003.

**REPORT DOCUMENTATION PAGE (SF298)**  
**(Continuation Sheet)**

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P.L. Garrity, V. Reddy and K.L. Stokes, “Experimental and theoretical study of  $\text{Bi}_2\text{Te}_3$  nanocomposites,” in preparation for J. Appl. Phys.

**5. SCIENTIFIC PERSONNEL**

**Kevin Stokes**, Associate Professor of Physics

**Charles O'Connor**, Professor of Chemistry

**Jiye Fang**, Assistant Professor of Chemistry

**Feng Chen**, Senior Postdoctoral Research Associate (Physics)

**Ven Reddy**, Senior Postdoctoral Research Associate (Chemistry)

**Kyung-Sang Cho**, Postdoctoral Research Associate (Chemistry)

**Wolfgang Gaschler**, Postdoctoral Research Associate (Chemistry)

**Pat Garrity**, Graduate Research Assistant (Physics)

*Received MS in Physics, December 2003*

**Amar Kumbhar**, Graduate Assistant (Chemistry)

*Received MS in Chemistry, May 2001*

**Steven Dennis**, Graduate Assistant (Physics) 1 June 1999 to Sept. 2000

**Laurie Kelly**, Undergraduate Research Assistant (Physics)

**Kurt Reynolds**, Undergraduate Research Assistant (Physics)

**REPORT DOCUMENTATION PAGE (SF298)**  
**(Continuation Sheet)**

**Chris Murray**, Manager, Nanoscale Materials and Devices, IBM T.J. Watson Research Center. Dr. Murray received no direct support from this grant; however, he was an integral part of this project and served as research supervisor to Dr. Cho and Dr. Gaschler through an IBM-UNO Joint Study Agreement.

**6. INVENTIONS**

Patent application in progress from 2003: *Chemical synthesis of bismuth-antimony alloy nanometer-scale particles*. J. Fang and K.L. Stokes.